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IMPREGNATED FIBROUS MATERIAL

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This invention relates to impregnated fibrous materials and, more particularly, to fibrous materials saturated with asphaltic compositions.

Heretofore fibrous materials have been saturated with various bituminous materials such as soft coal tar pitch, residual oil, soft residual asphalt, and soft blown asphalt. Occasionally, there has been employed mixtures of asphalt and tar, blends of asphalt, tar or pitch with rosin, paraffin oil, or mineral oil. Another group of materials which has been employed comprises bituminous materials blended with small amounts of substances termed "introfiers" which markedly increase the fluidity of the hot saturant and improve its wetting properties towards the materials being saturated, thereby increasing the speed of penetration. As introfiers there have been employed substances of the type of naphthalene, pyridine bases, nitrogenous distillation products such as bone oil, various diphenyl and triphenyl products, coumarone resins, etc. Numerous disadvantages attend the use of the prior art saturants. For example, the resulting product does not have the desired flexibility, is unduly susceptible to temperature changes, is too expensive, etc.

It is an object of the present invention to provide a fibrous material saturated with an asphaltic material and exhibiting improved properties.

Another object is to provide an improved method for saturating fibrous materials.

Another object is to enable the use of relatively high melting point blown petroleum asphalt in the saturation of fibrous materials by the hot melt process.

Other such objects will hereinafter appear.

I have discovered that the foregoing objects may in general be accomplished by saturating a fibrous material with a blend of an asphaltic material and a liquid ester of a rosin acid selected from the group consisting of abietic acid or hydrogenated abietic acid, the blend having a melting point (ring and ball) of at least about 100° F.

I have further discovered that by blending with a liquid ester of abietic acid or hydrogenated abietic acid, I may use as the asphaltic constituent blown petroleum asphalt having a melting point of at least about 140° F. and still get excellent results. The use of a petroleum asphalt blown to a sufficiently high softening point to give satisfactory weathering characteristics has been known to be desirable but has been impractical because of the fact that the time required for saturation is very long and the quantity of saturant taken up by the fibrous material is too small. However, by blending such a blown petroleum asphalt with esters of the present invention, these disadvantages which have restricted the use of blown asphalt of high melting point in the impregnation of fibrous materials are overcome.

As the liquid rosin or hydrogenated rosin ester, I may employ esters with lower aliphatic alcohols such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, iso-amyl, allyl, etc., with the glycols and especially those glycols which have an ether linkage such as diethylene glycol and triethylene glycol, with aromatic compounds such as phenol, alpha-naphthol, beta-naphthol, with aralkyl alcohols like benzyl alcohol, with alicyclic alcohols such as cyclohexanol, and other alcohols which yield liquid esters of rosin or hydrogenated rosin (abietic acid or hydrogenated abietic acid). I use a rosin ester or hydrogenated rosin ester which is a resinous liquid at ordinary temperature (20° C.). I prefer to use methyl abietate or hydrogenated methyl abietate.

As the fibrous material, I may employ any of the conventional used materials such as asbestos paper, felt, and felted fabrics in general, prepared board such as fiber board, woven fabrics such as for example cotton fabrics and the like. The fibrous material is preferably in the form of a sheet of the type commonly used in this art. The fibrous sheet material may be of any desirable thickness such as is commonly employed in the art. For example, I may use such fibrous bases as are commonly employed in the preparation of sheet roofing, floor coverings, waterproofing membranes, insulating and building papers, and the like. The resulting saturated fibrous sheet may be employed where electrical insulating characteristics are desired.

The fibrous material may be impregnated with the blend in any suitable manner as for example by running the preformed web through a tank of the molten saturant. Preferably, the saturant is at a temperature substantially above its melting point. The tank may be under elevated pressure, under vacuum, or at atmospheric pressure with such mechanical adjuncts as corrugated rolls, scrapers, or vertical stacks of steam heated rolls through which the saturated web passes.

An advantage of the use of compositions of the present invention in the preparation of saturated fibrous materials is the greater speed of impregnation. A further advantage is that this greater

speed of impregnation is obtained by other than mechanical means so that the expense of the installation is not increased. Another advantage is that the process of the present invention permits the saturation of the fibrous material at lower temperatures so that there is less injury to the strength of the board or other fibrous sheet, with the result that a product of higher strength is obtained.

As the asphaltic material, I may employ a material giving a blend having a melting point (ring and ball) of at least about 100° F., such as; native asphalts; asphaltites like gilsonite, grahamite or the like; asphaltic pyrobitumens such as elaterite, wurtzilite; etc.; petroleum asphalts such as straight run petroleum asphalt, steam distilled petroleum asphalt, pressure tar, sludge asphalt, blown petroleum asphalt, etc. I prefer to use blown petroleum asphalt having a ring and ball melting point of at least about 140° F.

The asphaltic material is fluxed or plasticized with from about 1% to about 10% by weight based on the weight of the blend, of the liquid ester of abietic acid or hydrogenated abietic acid. Preferably the saturant contains no or substantially no volatile materials.

The addition of relatively small amounts of the liquid resinous esters of the present invention to the asphaltic material lowers the viscosity of the saturant when molten and greatly increases its speed of penetration into the fibrous material. This increased speed of penetration into the fibrous material may be due to the improved wetting action contributed by the liquid abietic or hydrogenated abietic ester. In addition, the invention permits the use of lower impregnation temperatures without increasing the time required. The lowering of viscosity effected is much greater than the lowering of melting point of the asphaltic material, which is advantageous since it permits more rapid and more effective impregnation of the fibrous material without decreasing the hardness of the solidified impregnant.

The esters employed in accordance with the present invention possess very desirable electrical characteristics so that their use does not detract from the insulating powers of the resulting impregnated fibrous material. Since the esters are non-volatile, exhibiting an extremely low vapor pressure at high temperatures, and since they are highly resistant to heat the saturating blend may be maintained in the hot molten condition for indefinite periods of time. Because the composition contains no volatile components and because of the high flash point of the esters employed, no appreciable increase in fire hazard is involved in the application of the principles of the invention. In addition, the resulting product has greater flexibility and impact strength when cold for a given melting point of the blend. Since the esters employed in accordance with the present invention cannot be saponified by ordinary methods, the resulting impregnated fibrous materials are highly resistant to the action of alkalies. This is especially advantageous where the products are used in the manufacture of floor covering or the like.

In the following table, there are summarized the results of a series of runs in which asbestos paper and felt were saturated with a blend of blown asphalt with from 1% to 7% of each of methyl abietate and hydrogenated methyl abietate, the blend being held at 450° F. The times given are those required to effect complete saturation. The felt was a mixture of cellulose and wool fibers such as is used in floor coverings and known in the trade as "felt base."

Type of asphalt	Time required to saturate felt	Decrease in time required to saturate felt	Time required to saturate asbestos paper	Decrease in time to saturate asbestos paper
Blown asphalt 180°/200° F.	*Seconds* 45	*Per cent*	*Min. Sec.* 4 30	*Per cent*
Ditto but blended with 1% of hydrogenated methyl abietate	40	11	3	33⅓
Ditto but blended with 1% of methyl abietate	40	11	3	33⅓
Ditto but blended with 4% of hydrogenated methyl abietate	35	22	2 20	48
Ditto but blended with 4% of methyl abietate	35	22	2 15	50
Ditto but blended with 7% of hydrogenated methyl abietate	30	33⅓	2	55
Ditto but blended with 7% of methyl abietate	30	33⅓	2	55

While the foregoing table indicates that the times for saturation with the unhydrogenated esters are approximately the same as those for the hydrogenated esters, nevertheless, I prefer to use the hydrogenated esters because they are essentially non-reactive with oxygen and therefore yield a more stable product.

The addition of the esters of the present invention to asphaltic materials results in greatly increased fluidity at temperatures above the melting point of the bituminous material without correspondingly decreased melting point. The following table shows the effective reduction in viscosity brought about by blending from 1 to 10% of methyl abietate or hydrogenated methyl abietate with untreated blown asphalt having a drop melting point of 206° F. (this was the asphalt indicated in the above table as having a melting point of 180°/200° F.). The viscosities in this table were determined by means of the Koppers viscometer at 178° C. The percentage reduction in viscosity was calculated on the viscosity of the unmodified asphalt as compared to the blends.

Amount and type of liquid ester added	Drop M. P.	Reduction in viscosity
	°F.	*Per cent*
Blank, no modifying agent	206	
1% hydrogenated methyl abietate	201	17.8
1% methyl abietate	203	11.3
4% hydrogenated methyl abietate	188.6	44.6
4% methyl abietate	192.2	43.5
7% hydrogenated methyl abietate	183.5	59.2
7% methyl abietate	185	59.1
10% hydrogenated methyl abietate	174	68.5
10% methyl abietate	176.5	70

In preparing the hot melt saturant to be used in accordance with the present invention, I prefer to heat the asphaltic material to from about 50° F. to about 150° F. above its melting point and then to add slowly the liquid abietic ester with thorough stirring. In making up the compositions described above, the air blown petroleum asphalt, having a ring and ball melting point of 180°/200° F. and obtained from the Socony Vacuum Oil Company, was heated to 300° F. whereupon the required amount of the liquid resin was admixed therewith with thorough stirring.

In addition to the runs described in connec-

tion with the first table above, the following runs were made.

Examples 1 to 3

Felt was saturated with blends of air blown petroleum asphalt having a ring and ball melting point of 180°/200° F. with ethyl abietate in the respective proportions of 99 parts asphalt and 1 part ethyl abietate, 96 parts asphalt and 4 parts ethyl abietate, and 93 parts asphalt and 7 parts ethyl abietate.

Examples 4 to 11

Felt of the type used as the base for roofing was saturated with blends of steam reduced asphalt of a ring and ball melting point of 160°/170° F. with methyl abietate and hydrogenated methyl abietate in the proportions indicated in the following table:

Example No.	4	5	6	7	8	9	10	11
Parts asphalt	99	96	93	90	99	96	93	90
Parts methyl abietate	1	4	7	10	--	--	--	--
Parts hyd. methyl abietate	--	--	--	--	1	4	7	10

Impregnation with these blends heated to 450° F. gave a much faster saturation than with the straight asphalt heated to 450° F. For example the blend of Example 9 required only 35 seconds to completely saturate the felt whereas the straight asphalt required 40 seconds. Similar figures were obtained with the other blends of Examples 4 to 11, and similar reductions were noted with all of the blends of Examples 4 to 11 in the impregnation of asbestos paper.

Example 12

Fiberboard core stock 3/8" thick was impregnated with asphaltic saturant alone and blended with methyl abietate at the temperatures indicated below. The indicated times were required for complete penetration. The asphaltic saturant used was obtained directly from the refinery.

Temperature of saturant	Saturant used	Time of saturation
		Minutes
390° F.	Unblended asphalt	17.5
390° F.	Asphalt+2% methyl abietate	14.0
375° F.	Asphalt+2% methyl abietate	15.5
390° F.	Asphalt+4% methyl abietate	12.5
375° F.	Asphalt+4% methyl abietate	14.5
365° F.	Asphalt+4% methyl abietate	16.5

These results indicate that a saving in time of impregnation, a lowering of the impregnation, or both, may be brought about by the addition of methyl abietate. Equivalent results are obtained with hydrogenated methyl abietate.

Instead of commingling the liquid ester of abietic acid or hydrogenated abietic acid with the asphaltic material in advance in the manner set forth in the foregoing, I may obtain similar results by commingling these materials in situ, i. e. within the fibrous material being impregnated. This may be accomplished by impregnating the fibrous material with the liquid resinous ester followed by saturation with the hot molten asphaltic material. In this way, the speed of impregnation with the asphaltic material is considerably increased.

In order to effect the preliminary impregnation of the fibrous material with the liquid ester, I may prepare a dilute aqueous oil-in-water type emulsion of the liquid ester containing from about 0.5% to about 5% of the ester, soak the fibrous material in this emulsion, and dry to remove the water. Or I may impregnate the fibrous material with a dilute solution of the liquid ester in a volatile organic solvent containing from 0.5% to about 5% of the ester.

Following are examples of a series of runs embodying the preliminary impregnation of the fibrous material with the liquid ester in the manner just described followed by the impregnation in the asphalt.

Examples 13 to 20

Methyl abietate and hydrogenated methyl abietate were emulsified in an equal weight of water containing 1.2% of sulfonated castor oil and 1.2% of "Duponol Me" (the sodium salt of sulfonated lauryl alcohol). This emulsion was diluted with water to the concentration shown in the following table. Fiberboard core stock 3/8" thick was then soaked in the emulsion until impregnation was complete, dried at 210–220° F. for several hours to remove the water, and impregnated with asphalt at a temperature of 390° F. The results are given in the table. An unimpregnated blank required 16 minutes for saturation with the asphalt.

Example No.	Concentration of liquid ester in emulsion	Liquid ester deposited in board based on weight of board	Liquid ester in board after saturation with asphalt based on asphalt	Time of saturation
		Per cent	*Per cent*	*Minutes*
13	3% hydrogenated methyl abietate	5.0	2.26	12
14	1% hydrogenated methyl abietate	3.25	1.48	14
15	0.5% hydrogenated methyl abietate	2.3	1.02	14
16	4% methyl abietate			11.5
17	3% methyl abietate	6.25	3.0	12.5
18	1% methyl abietate	3.14	1.3	13.5
19	0.5% methyl abietate	3.0	1.28	14

From the foregoing it will be seen that the use of the abietic and hydrogenated abietic acid esters of the present invention in conjunction with asphaltic materials such as blown asphalt in the saturation of fibrous materials such as asbestos, felted fibrous sheet materials, and the like gives rise to a number of very desirable advantages over the prior art compositions.

It will be understood that the details and examples hereinbefore set forth are illustrative only and that the invention as broadly described and claimed is in no way limited thereby.

What I claim and desire to protect by Letters Patent is:

1. The process which comprises impregnating a fibrous material with a liquid ester of a rosin acid selected from the group consisting of abietic acid and hydrogenated abietic acid, and thereafter saturating the fibrous material so impregnated with an asphaltic material.

2. The process which comprises impregnating a fibrous material with a lower aliphatic ester of a rosin acid selected from the group consisting of abietic acid and hydrogenated abietic acid, and thereafter saturating the fibrous material so impregnated with an asphaltic material.

3. The process which comprises impregnating a fibrous material with a methyl ester of a rosin acid selected from the group consisting of abietic acid and hydrogenated abietic acid, and thereafter saturating the fibrous material so impregnated with an asphaltic material.

4. The process which comprises impregnating an asbestos paper with a methyl ester of a rosin acid selected from the group consisting of abietic acid and hydrogenated abietic acid, and thereafter saturating the asbestos paper so impregnated with an asphaltic material.

5. The process which comprises impregnating felted cellulose fibers with a methyl ester of a rosin acid selected from the group consisting of abietic acid and hydrogenated abietic acid, and thereafter saturating the felted cellulose fibers so impregnated with an asphaltic material.

6. The process which comprises impregnating felted wool fibers with a methyl ester of a rosin acid selected from the group consisting of abietic acid and hydrogenated abietic acid, and thereafter saturating the felted wool fibers so impregnated with an asphaltic material.

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